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Phonon Relaxation and Line Shapes of Adsorbates

by

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PHONON RELAXATION AND LINE SHAPES OF ADSORBATES

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1. Introduction

When an atom or molecule is adsorbed on the surface of a solid, a variety of processes may occur. Most extensively studied, because of practical applications, is the interaction between a diatomic molecule and a metal substrate. Such molecules bind very strongly to the surface, and the molecular wave functions extend into the metal (chemisorption). This leads to electron-hole pair formation of conduction electrons (charge transfer from the molecule to the metal), which gives rise to thermal relaxation of the adsorbate (Rantala and Rosen 1986, Volokitin et al 1986, Morawitz 1987). Besides this electronic decay, the internal molecular stretching mode can also couple kinetically to the motion of the crystal atoms. Effectively, vibrational internal energy of an excited molecule can be converted into kinetic energy of the lattice atoms (phonons), which provides a second thermal decay channel for the adsorbate (Casassa et al 1986, Beckerle et al 1990). In model calculations it is

usually assumed that the molecular kinetic degrees of freedom couple to the bulk vibrational modes of the crystal. In certain situations, however, a molecular resonance can coincide with the peak in the surface-phonon dispersion relation. Thermal relaxation is then dominated by kinetic coupling to surface phonons, rather than to bulk phonons (van Smaalen and George 1987, Dumas et al 1990). Also, migration of the molecules over the surface of the solid might affect the relaxation mechanism (Efrima and Metiu 1978, Persson and Hoffmann 1988), and when the adsorbates form a gas-solid interface, equilibrium with the desorption channels should be taken into account. When the experiment is performed in vacuum, thermal desorption leads to a loss of molecules, which does not affect the relaxation of the remaining molecules.

We shall consider the most simple situation of an atom (no internal modes), adsorbed on the surface of a dielectric crystal. Then the atom will be bound to the surface by a van der Waals potential, which has a width of the order of 1 Å, and is in good approximation a Morse potential (Chou and Chelikowsky 1987, Muller 1990). Thus the atom is entirely outside the crystal (physisorption), and overlap of electronic wave functions can be neglected. As a further simplification, we shall assume that the motion of the atom (mass m) is restricted to the direction perpendicular to the surface, and that the bond is brought about by a van der Waals interaction with the nearest crystal atom (mass M) only. With \vec{u} the position operator of M with respect to its equilibrium position, and $z\vec{e}_z$ the position operator of m , the interaction

potential $V(r)$ depends on the distance $r = |\vec{z}\vec{e}_z - \vec{u}|$ between m and M (fig. 1).

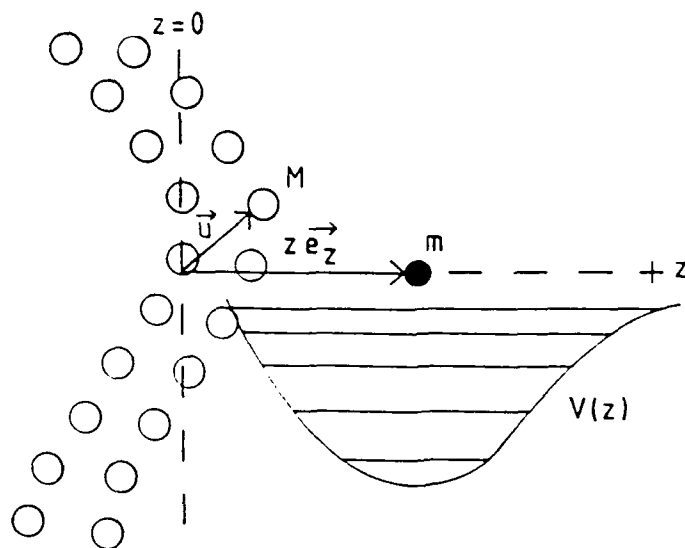


Fig. 1. Pictorial representation of an atom with mass m near a solid in $z < 0$, consisting of atoms with mass M . The plane $z = 0$ is the thermal equilibrium position of the surface, and the atom m is located on the positive z -axis.

The amplitude of vibration of M is of the order of 0.1 \AA , which is much smaller than the average value of z . Therefore we can make a Taylor expansion of $V(r)$ around $r = z$, or equivalently, $\vec{u} = 0$. This yields

$$V(r) = V(z) - (\vec{u} \cdot \vec{e}_z) \frac{dV}{dr}(r = z) . \quad (1.1)$$

The operator \vec{u} is linear in the creation and annihilation operators for phonons, and consequently the omission of higher-order terms in the expansion (1.1) has the effect of neglecting single-step multiphonon transitions between the adsorbate bound states. For a Morse potential such an approximation is not necessary, and it has been shown by model calculations that multiphonon

transitions play a negligible role indeed, provided that the resonances of the adbond (atom in potential well) are well below the Debye frequency ω_D of the crystal.

2. Relaxation

For the Hamiltonian of the system we can write

$$H = H_a + H_p + H_{ap} . \quad (2.1)$$

Here, H_a represents the adbond Hamiltonian, consisting of the kinetic energy of m and the potential $V(z)$ from eq. (1.1). The Hamiltonian H_p represents the phonons of the crystal, and thereby the motion of M . The interaction between the adsorbate and M is accounted for by H_{ap} , which equals the second term on the right-hand side of eq. (1.1). With σ an arbitrary operator, the corresponding Liouvillians are defined as

$$L_i \sigma = \hbar^{-1} [H_i, \sigma] , \quad i = a, p, ap , \quad (2.2)$$

and the equation of motion for the density operator ρ of the system attains the form

$$i \frac{d\rho}{dt} = (L_a + L_p + L_{ap}) \rho . \quad (2.3)$$

The equation of motion (2.3) describes the time evolution of the adbond, and of every atom in the crystal through the phonon field. We are interested in the adsorbate part of $\rho(t)$, which is defined as

$$\rho(t) = \text{Tr}_p \rho(t) , \quad (2.4)$$

where the trace runs over all phonon states. An equation of motion for the reduced density operator $\rho_a(t)$ is usually derived with standard reservoir

theory, in which the phonon field of the crystal is considered as a thermal reservoir with equilibrium density operator $\bar{\rho}_p$. This $\bar{\rho}_p$ can be taken as

$$\bar{\rho}_p = N \exp(-H_p/k_B T) , \quad (2.5)$$

in terms of the temperature T and Boltzmann's constant k_B . The normalization factor is $N = \text{Tr}_p \exp(-H_p/k_B T)$. Then, $\bar{\rho}_p$ will not be affected by the few atoms on the surface. However, the time evolution of $\rho_a(t)$ is influenced by phonon-exchange interactions between the adbond and the crystal. Effectively, this gives rise to thermal relaxation of the adbond towards thermal equilibrium with the crystal.

With standard reservoir theory, the reservoir enters the equation of motion for $\rho_a(t)$ parametrically through the correlation function

$$f(\tau) = \hbar^{-2} \text{Tr}_p \bar{\rho}_p u_z e^{-iL_p \tau} u_z , \quad (2.6)$$

for the case where the interaction is given by eq. (1.1). The relaxation constants, which are the matrix elements of the relaxation operator, can be expressed in terms of the Fourier-Laplace transform

$$\tilde{f}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} f(\tau) , \quad (2.7)$$

and with ω equal to resonance frequencies of the adbond (level separations in fig. 1). Both $f(\tau)$ and $\tilde{f}(\omega)$ can be evaluated explicitly (Arnoldus et al 1989). The behavior of $f(\tau)$ is illustrated in fig. 2, and fig. 3 gives the corresponding $\tilde{f}(\omega)$.

A common approximation in reservoir theory is the Markov approximation, in which it is assumed that the reservoir response time to perturbations is

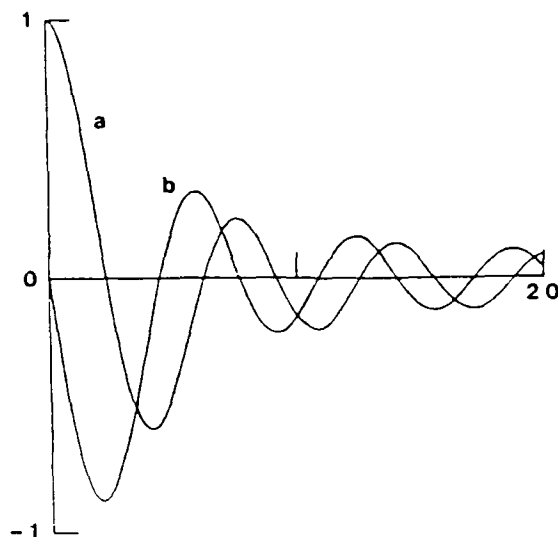


Fig. 2. Real (a) and imaginary (b) parts of the reservoir correlation function $f(r)$, multiplied by $2\kappa M \omega_D / 3$, for a harmonic crystal and zero temperature. The horizontal variable is $\omega_D \tau$.

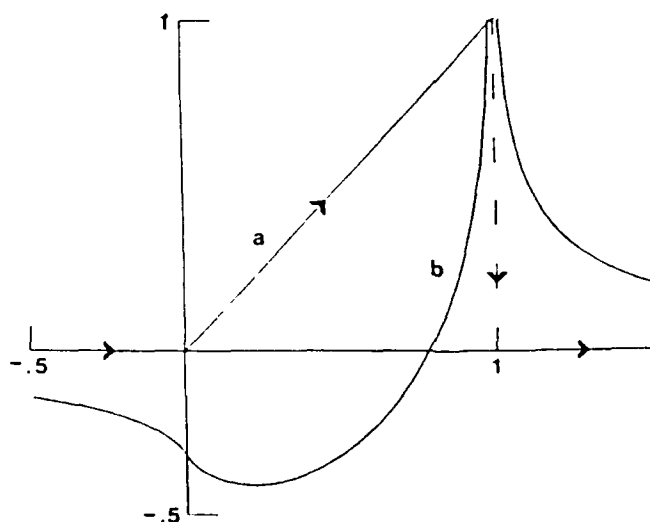


Fig. 3. Real (a) and imaginary (b) parts of the Fourier-Laplace transform $\tilde{f}(\omega)$ of the function $f(r)$ from Fig. 2. The horizontal variable is ω / ω_D , and the vertical variable is scaled with a factor $2\kappa M \omega_D^2 / 3$. For $\omega < 0$ and $\omega > \omega_D$ the real part vanishes identically. The imaginary part has a singularity at $\omega = \omega_D$, due to the sharp cutoff of the dispersion relation at the Debye frequency. For finite temperatures there is also a singularity at $\omega = -\omega_D$ (van Hove singularities).

very short compared to the relaxation times that are induced by the reservoir in the system (the adbond). This response time is the decay time of the function $f(\tau)$. Due to the cutoff of the phonon dispersion relation at ω_D , $\tilde{f}(\omega)$ has a cutoff at ω_D , as shown in fig. 3. Its inverse $f(\tau)$ therefore decays in a time $\tau \sim 1/\omega_D$, as illustrated in fig. 2. It turns out that for phonon relaxation of adsorbates, relaxation constants can have the same order of magnitude as ω_D , which invalidates a Markov approximation. An additional complication is that an adbond resonance frequency can be larger than ω_D , in which case Markovian reservoir theory does not apply at all. In order to resolve these problems, we have developed a generalized finite-memory-time reservoir theory which puts no restrictions on the decay time of $f(\tau)$ and the order of magnitude of the decay constants and the relevant frequencies (Arnoldus and George 1987). It appeared that the relaxation in the equation of motion could again be expressed entirely in terms of $\tilde{f}(\omega)$, but now $\tilde{f}(\omega)$ appears for all ω , rather than only at the adsorbate resonances. For the Fourier-Laplace transform of $\rho_a(t)$, we obtained the formal result

$$\tilde{\rho}_a(\omega) = \frac{i}{\omega - L_a + i\Gamma(\omega)} \rho_a(0), \quad (2.8)$$

for a given initial value $\rho_a(0)$. The relaxation operator $\Gamma(\omega)$ is given by

$$\Gamma(\omega)\sigma_a = \text{Tr}_p L_{ap} \frac{i}{\omega - L_a - L_p} L_{ap} (\sigma_a \bar{\rho}_p), \quad (2.9)$$

where σ_a is an arbitrary adbond operator, and the trace runs over phonon states only. Matrix elements of the (Liouville) operator $\Gamma(\omega)$ can be evaluated explicitly in terms of $\tilde{f}(\omega)$ and matrix elements of dV/dz (Arnoldus

and George 1988a). When eq. (2.8) is transformed to the time domain, then the ω -dependence of $\Gamma(\omega)$ gives rise to a memory in the time evolution of $\rho_a(t)$. The memory kernel is the Fourier-Laplace inverse of $\Gamma(\omega)$, which is proportional to $f(\tau)$.

The time evolution of $\rho_a(t)$ does not have much relevance, because due to the relaxation, the operator $\rho_a(t)$ will approach its thermal-equilibrium value $\bar{\rho}_a$ quickly. From eq. (2.8) it follows that $\bar{\rho}_a$ is the solution of

$$(L_a - i\Gamma(0))\bar{\rho}_a = 0. \quad (2.10)$$

Apparently, the steady-state density operator is determined by $\Gamma(\omega)$ at $\omega = 0$ only. This $\Gamma(0)$ is different from its Markovian equivalent.

3. Absorption Profile

The measurement of $\bar{\rho}_a$ (level populations) would provide information about the relaxation constants which make up the matrix $\Gamma(0)$, but it does not reveal the dynamical interaction mechanism between the adsorbate and the crystal. Dynamical features of the system do not only determine the time evolution of the density operator, but also the time regression of quantum operators in the Heisenberg picture. For instance, correlation functions of the dipole moment $\vec{u}(t) = \mu(t)\vec{e}_z$ determine the photon absorption profile of the adbond. When a low-intensity infrared laser with frequency ω irradiates the system, then the absorbed energy per unit of time is given by

$$I(\omega) = \omega \operatorname{Re} \lim_{t \rightarrow \infty} \int_0^\infty d\tau e^{i\omega\tau} \operatorname{Tr} \rho(t) [\mu(t+\tau), \mu(t)]. \quad (3.1)$$

Here, an overall constant has been suppressed. In the Schrödinger picture, this becomes

$$I(\omega) = \omega \operatorname{Re} \int_0^\infty dr \operatorname{Tr} \mu e^{i(\omega-L)r} [\mu, \bar{\rho}] , \quad (3.2)$$

with $L = L_a + L_p + L_{ap}$. Hence the exponential which governs the time regression is identical to the time evolution operator of the density operator $\rho(t)$ of the system (see, eq. (2.3)). Consequently, the absorption profile carries information about the dynamics of the adbond system, and this is directly amenable for experimental observation (Chabal and Sievers 1980).

Expression (3.2) can be evaluated with finite-memory-time reservoir theory. The formal result is

$$I(\omega) = \omega \operatorname{Re} \operatorname{Tr}_a L_x \frac{i}{\omega - L_a + i\Gamma(\omega)} (L_y - iT(\omega)) \bar{\rho}_a , \quad (3.3)$$

where the trace runs over adbond states only. The Liouvillians L_x and L_y are defined by

$$L_x \sigma_a = \mu \sigma_a , \quad (3.4)$$

$$L_y \sigma_a = [\mu, \sigma_a] . \quad (3.5)$$

In eq. (3.3), the inverse operator following L_x is the same as in eq. (2.8) for the time evolution of $\rho_a(t)$. Again, a memory effect on $I(\omega)$ is reflected in the frequency dependence of the relaxation operator $\Gamma(\omega)$. Furthermore, we have a term with $T(\omega)$, which is absent in a Markov approximation. It can be shown that this term arises due to the fact that the steady-state density operator $\bar{\rho}$ of the entire system does not factorize as $\bar{\rho}_a \bar{\rho}_p$. We call $T(\omega)$ the initial-correlation operator, since it accounts for correlations between the

adbond and the phonons at time $t = 0$ in eq. (3.2). The Liouville operator $T(\omega)$ is found to be

$$T(\omega)\sigma_a = \text{Tr}_p L_{ap} \frac{i}{\omega - L_a - L_p} L_y \frac{1}{i0^+ - L_a - L_p} L_{ap}(\sigma_a \bar{\rho}_p), \quad (3.6)$$

and its matrix elements can be expressed in terms of $\bar{f}(\omega)$ and matrix elements of dV/dz . The result, however, is cumbersome (Arnoldus and George 1988a).

4. Line Shape

The absorption profile $I(\omega)$ acquires contributions from all adbond transitions, and interferences between these. In order to illustrate some important properties of $I(\omega)$, we consider the situation where the potential well supports only two bound states. Let $|1\rangle$ be the lowest state, $|2\rangle$ the excited state, and ω_0 the frequency separation between them. We also define a dipole parameter

$$m = \left[\frac{\mu_{22} - \mu_{11}}{\mu_{21}} \right]^2, \quad (4.1)$$

which measures the difference in permanent dipole moments of the two states, relative to their transition dipole moment μ_{21} . Then it is straightforward to evaluate $I(\omega)$ explicitly, but the expression is not very illuminating. Figures 4 and 5 show two representative profiles, although the line widths are highly exaggerated (for illustrative purposes). In a Markovian theory, the line shape is a Lozentzian, which is symmetric around a frequency close to ω_0

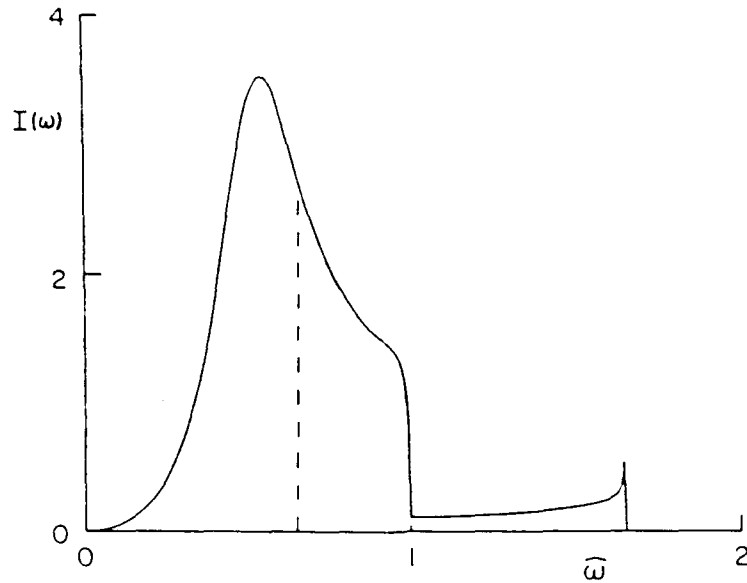


Fig. 4. Absorption profile $I(\omega)$ as a function of $\hat{\omega} = \omega/\omega_D$. The adbond resonance is located at $\hat{\omega} = 0.65$ (dotted line), and the dipole parameter is $m = 0.7$.

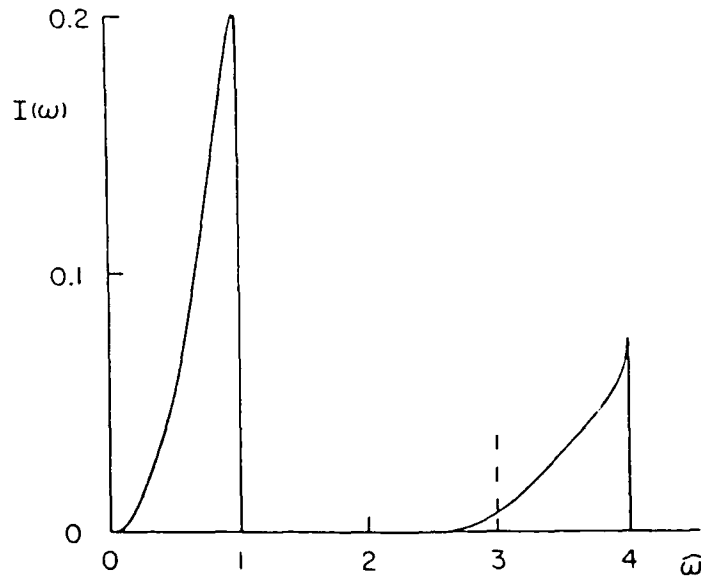


Fig. 5. Absorption profile for the same parameters as in fig. 4, except that here $\hat{\omega}_0 = 3$. Notice the different scale on the vertical axis.

(there is only one relaxation constant in the Markov approximation: its real part is the line width at half maximum and its imaginary part equals the shift from ω_0). Figure 4 shows a typical case for $\omega_0 < \omega_D$. The big peak around the dotted line comes from the term proportional to L_y in eq. (3.3), and it is very close to the Markovian Lorentzian for $\omega < \omega_D$ (in fact, they coincide within drawing accuracy). It can be shown analytically that this L_y -contribution to $I(\omega)$ is identically zero for $\omega > \omega_D$, due to the ω -dependence of the relaxation operator $\Gamma(\omega)$, e.g., due to memory effects. The small peak at $\omega > \omega_D$ comes from the term proportional to $T(\omega)$, and is therefore entirely due to memory effects. We called this a memory-induced extra resonance (Arnoldus and George 1988b). This part of the spectrum is proportional to the parameter m , and therefore requires a permanent dipole moment. Figure 5 gives $I(\omega)$ for $\omega_0 > \omega_D$. The peak on the left is the tail of the Lorentzian around ω_0 , cut off at $\omega = \omega_D$. The peak on the right is the memory-induced line, which has a cutoff at $\omega = \omega_0 + \omega_D$.

The physical explanation for the various properties of the line shape is illustrated in fig. 6. Diagram (a) is an elastic photon-phonon conversion, responsible for the L_y -part of the spectrum, which becomes a Lorentzian in the Markovian approximation. A photon is absorbed from the laser, and subsequently converted into a phonon, which is emitted into the crystal. The reverse process, not shown, in which a phonon is absorbed and a photon is emitted, also occurs. The net absorption is the balance between the two processes. Then it is obvious that these processes do not happen for $\omega > \omega_D$,

because there are no phonons with a frequency larger than ω_D . Diagrams (b) and (c) show the processes for the memory-induced line. It follows immediately from the figure that these processes can only occur for $|\omega - \omega_0| < \omega_D$, which explains the cutoff of this line at $\omega_0 + \omega_D$. The reverse processes, not shown, also contribute. These are stimulated emissions of photons by the adbond into the laser field, and the initial state for these diagrams is $|2\rangle$, rather than $|1\rangle$.

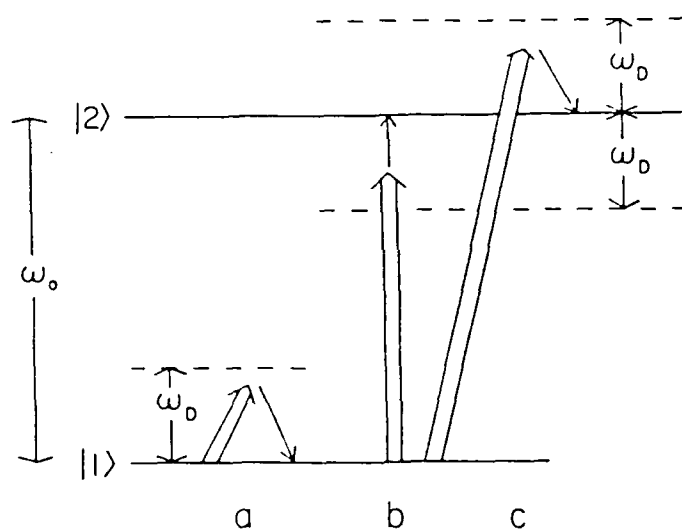


Fig. 6. Energy-conserving diagrams which contribute to the absorption profile for a two-state system. A double-line arrow represents a photon, and a single-line arrow corresponds to a phonon. The reverse processes, with $|2\rangle$ as initial state, are not shown.

5. Conclusions

We have studied the spectral line shape of an adsorbed atom on the surface of a crystal. Phonon exchange interactions between the adbond and the crystal are responsible for the formation of the line shape. It was shown that Markovian reservoir theory, which predicts a Lorentzian line shape, is inadequate in general, due to the fact that the Debye frequency is of the same order of magnitude as the adbond transition frequencies. Finite-memory-time reservoir theory takes into account properly this low cutoff of the dispersion relation, and it provides closed-form analytical expressions for the line shape. It appears that the spectral profile drops to zero identically for $\omega > \omega_D$. In addition, a memory-induced line appears around $\omega_0 + \omega_D$. Recently, Georgievskii and Stuchebrukhov (1990) have found very similar results by a direct numerical integration of the Schrödinger equation.

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